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ON THE THEORY OF THE RATE OF CRYSTALLIZATION PROCESSES AT DECREASING CONCENTRATION OF THE CRYSTALLIZING SUBSTANCE IN A HOMOGENEOUS PHASE

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-USSR-

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FOREWORD

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ON THE THEORY OF THE RATE OF CRYSTALLIZATION PROCESSES AT DECREASING CONCENTRATION OF THE CRYSTALLIZING SUBSTANCE IN A HOMOGENEOUS PHASE

- USSR -

/Following is a translation of the article entitled "K teorii skorosti kristallizatsionnykh protsessov pri padayushchey kontsentratsii kristallizuyushchegosya veshchestva v gomogennoy faze" (English version above) by O. M. Todes in Isvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk (Proceedings of the Academy of Sciences, USSR, Division of Chemical Sciences), No 2/3, Moscow, 1942, pages 106-115./

In the crystallization process from vapor or from solution, the concentration in this homogeneous phase of the substance that is settling out continually decreases. Parallel with the consumption of the substance and the decrease of its concentration in the homogenous phase the rate of the further growth of the crystal particles already formed and the rate of formation of new nuclei -- crystallization centers -- also decrease. The latter rate decreases unusually sharply with decrease in supersaturation, and this circumstance greatly simplifies calculations in the analysis of the kinetics of the process. The method which we developed for the calculation of the kinetics of the crystallization (1) enabled us in this case very easily to elaborate forth all the fundamental characteristics of the process and the form of the distri-

bution curve. The latter exhibits a peaked nature (cf figure 3) and in form is similar to the Gaussian error distribution curve.

1. The fundamental equation of the process

In one of our previous studies (1) devoted to the kinetics of crystallization, we developed a fundamental equation for the provisional course of the process at decreasing concentration of the crystallizing substance in a homogeneous phase. In addition isothermal crystallization from solution or from the vapor state is studied in the practical absence of the settling out of the forming particles under the force of gravity, when the total volume of all the separating crystals occupies only a negligible portion of the bulk of the homogeneous phase.

We retain the symbols introduced in the previous studies (1,2): $x(t) = X(t) - x_0$ stands for the supersaturation, that is, the excess of the instantaneous concentration in the homogeneous phase $X(t)$ over the equilibrium concentration at the given conditions -- x_0; ρ is the density of the crystals; γ is the coefficient of the crystal form (the ratio of the crystal volume $\omega = \gamma l^3$ to the cube of its radius l); $\alpha(x)$ is the probability of the formation of a nucleus -- crystallization center -- per unit volume per unit time; and $\lambda(x) = dl/dt$ is the linear rate of crystal growth. We derive an auxiliary variable

$$z(t) = \int_0^t \lambda(x'')dt'' \quad , \tag{1}$$

which is the radius of the largest crystal at the moment of time t. Whence the radius of a crystal forming from a certain preceding moment t' to a given moment t will be equal to:

$$l_{tt'} = \int_{t'}^{t} \lambda(x'')dt'' = z(t) - z(t') = z - z' \tag{2}$$

and the volume of this crystal equal to:

$$\omega_{tt'} = \gamma l^3_{tt'} = \gamma[z - z']^3 . \tag{3}$$

The total volume of all the crystal particles separating out up to the moment t is equal to:

$$v(t) = \int_0^t \omega_{tt'}\alpha(x')dt' = \int_0^t \gamma\alpha(x')[z - z']^3 dt'$$

$$= \int_0^z \gamma \frac{\alpha(x')}{\lambda(x')} [z - z']^3 dz'. \quad (4)$$

In time dt the quantity of crystallized substance per unit volume increases by $\rho dv(t)$.

This expression must be equal to the decrease in concentration in the volume

$$\rho dv(t) = - dx(t). \quad (5)$$

Considering the quantity z introduced by us above in the capacity of an independent variable, we obtain the fundamental equation of the mass balance:

$$\frac{dx}{dz} = -\rho\gamma\frac{d}{dz}\int_0^z F(x')[z - z']^3 dz', \quad (6)$$

where $F(x) = \frac{\alpha(x)}{\lambda(x)}$. (7)

Differentiating both parts of equation (6) three times with respect to z, we obtain the final equation of the process:

$$\frac{d^4x}{dz^4} = - 6\gamma\rho F(x) \quad (8)$$

with the initial conditions: at z = 0 (i. e., at t = 0)

$$x_0 = x_N; \left.\frac{dx}{dz}\right|_0 = \left.\frac{d^2x}{dz^2}\right|_0 = \left.\frac{d^3x}{dz^3}\right|_0 = 0. \quad (9)$$

The probability of nuclei formation $\alpha(x)$ (and, consequently, also the quantity F(x)) decreases unusually sharply with decrease in supersaturation. According to Volmer

$$\alpha(x) = A \exp\left\{- \frac{4\sigma^3\gamma v^2}{KT(\mu_1 - \mu_2)}\right\}; \quad (10)$$

here σ is the surface tension of the crystal,
v is the volume corresponding to the crystal per

single molecule,

T is the absolute temperature,

K is Boltzmann's constant,

$\mu_1 - \mu_2$ is the difference in the chemical potentials of the supersaturated and the equilibrium solutions.

For ideal solutions

$$\mu_1 - \mu_2 = KT\lg(x + x_o) - KT\lg x_o = KT\lg\left(1 + \frac{x}{x_o}\right). \quad (11)$$

At low relative supersaturation ($\frac{x}{x_o} \ll 1$):

$$\alpha(x) \cong Ae^{-c\frac{x_o^2}{x^2}} \quad (12')$$

and at high supersaturation ($\frac{x}{x_o} \gg 1$):

$$\alpha(x) \cong Ae^{-\frac{c}{\lg^2\left(\frac{x}{x_o}\right)}}, \quad (12'')$$

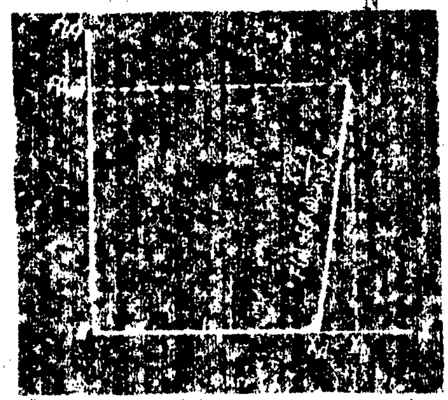
where $C = \frac{4\sigma^3\gamma v^2}{(KT)^3}$ is a dimensionless parameter, which usually has a numerical value of the order of several thousands. Both expressions (12') and (12") fall off quite sharply with decrease in supersaturation.

The function $F(x) = \frac{\alpha(x)}{\lambda(x)}$ behaves analogously to the probability of nuclei formation $\alpha(x)$ and also quite sharply diminishes with decrease in supersaturation. Therefore we can, to an approximation, replace the actual form of the curve $F(x)$ by the dashed line. At the beginning, with a small decrease in supersaturation, we can substitute for $F(x)$ the line which has the same slope as does the curve $F(x)$ at the initial point, $x = x_N$. At the point of the intersection of this line with the abscissa ($x = x_A$, cf figure 1) the value of $F(x)$ will be already small enough so that we can without large error consider this function equal to practically zero. Thus, the original equation (8) is broken into two equations corresponding to the two portions of the dashed line:

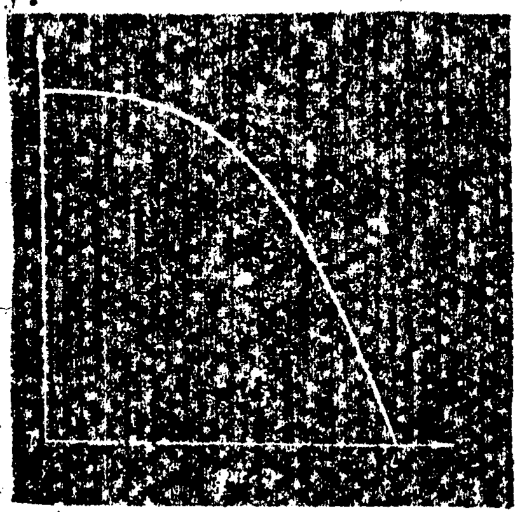
$$\frac{d^4x_I}{dz^4} = -6\gamma\rho F(x_N)\frac{x_I - x_A}{x_N - x_A} \quad \text{at } x_A \leqslant x \leqslant x_N, \quad (8')$$

$$\frac{d^4 x_{II}}{dz^4} = 0 \quad \text{at } 0 \leq x \leq x_A \,, \qquad (8'')$$

$$\text{where} \quad x_A = x_N - \frac{F(x_N)}{F'(x_N)} \,. \qquad (13)$$



At $x = x_A$ both solutions (8') and (8") must coincide with one another and also their derivatives up to the third order inclusively.



2. The analytic solution of the original equations

After some uncomplex, though somewhat cumbersome, calculations the desired solutions for equations (8') and (8") are easily obtained:

$$x_I(z) = x_A + (x_N - x_A)\cos\left(\frac{\pi}{2}\frac{z}{z_A}\right)\operatorname{coshyp}\left(\frac{\pi}{2}\frac{z}{z_A}\right), \qquad (14')$$

$$x_{II}(z) = x_A - \frac{1}{3}\cos\text{hyp}\,\frac{\pi}{2}\cdot(x_N - x_A)\left\{\left(\frac{\pi}{2}\,\frac{z - z_A}{z_A}\right)^3 + 3\,\text{tg hyp}\,\frac{\pi}{2}\cdot\left(\frac{\pi}{2}\,\frac{z - z_A}{z_A}\right)^2 + 3\left(\frac{\pi}{2}\,\frac{z - z_A}{z_A}\right)\right\}, \tag{14"}$$

$$\text{at } z = z_A = \frac{\pi}{2}\sqrt[4]{\frac{x_N - x_A}{1.5\gamma\rho F(x_N)}}\,. \tag{15}$$

Both solutions (14') and (14") and their derivatives up to the third order inclusively are in agreement. As seen from (7) and (8) this value of z corresponds to a practically complete cessation of crystallization. The probability of nuclei formation $\alpha(x)$ up to this moment decreases so sharply that the number of all the crystal particles forming up to the very end of the process, starting from the instant after the above-mentioned moment, is small enough that they can be neglected. z_A, consequently, is the maximum size of the crystals at the moment of the practical cessation of the formation of new nuclei of crystallization.

Since according to our assumptions $x_N - x_A \ll x_N$, then solutions (14') and (14") may be written approximately in the form:

$$x_I(z) \cong x_N - (x_N - x_A)\,\frac{\pi^4}{64}\left(\frac{z}{z_A}\right)^4, \tag{16'}$$

$$x_{II}(z) \cong x_A - (x_N - x_A)\frac{1}{3}\cos\text{hyp}\,\frac{\pi}{2}\left\{\frac{\pi}{2}\,\frac{z - z_A}{z_A}\right\}. \tag{16"}$$

The entire process of crystallization is completed at the moment when the supersaturation z decreases to zero. It is easy, thereupon, from (15") and (16") to calculate the size of the maximum crystal particles at the moment of completion of the process

$$z_{max} = L \cong \frac{2}{\pi}\,z_A\left\{\sqrt[3]{\frac{3x_A}{\cos\text{hyp}\,\frac{\pi}{2}(x_N - x_A)}} + 1 - \text{tghyp}\,\frac{\pi}{2}\right\} \cong \frac{2}{\pi}\,z_A\sqrt[3]{\frac{\quad}{\cos\text{hyp}\,\frac{\pi}{2}(x_N - x_A)}}\,. \tag{17}$$

Since $z_{max} \gg z_A$, then the solution of our fundamental equations practically from the very first can be set forth as equation (16"), or the latter almost cannot be distinguished from

$$x(z) \cong x_N - (x_N - x_A) \frac{\cos hyp \frac{\pi}{2}}{3} \left\{\frac{\pi}{2} \frac{z}{z_A}\right\}^3 = x_N\left\{1 - (\frac{z}{L})^3\right\}. \tag{18}$$

3. The fundamental characteristics of the process

Arising from the solutions obtained in the form of (14), (16), or (18), we can now calculate all the fundamental characteristics of the process and its time duration according to the scheme set forth in one of our preceding studies.

A. Distribution function

As was developed in our preceding studies, if the dependence of $x(z)$ is found, then the number of particles dn_{dl}, whose sizes are included in the interval from l to $l + dl$, is determined by the formula:

$$dn_{dl} = F(x_{(l_{max} - l)}dl) \text{ at } l < l_{max}$$

and (19)

$$dn_{dl} = 0 \qquad \text{at } l > l_{max}.$$

Substituting here the obvious (yavnyy) form of the approximate dependence which we used in setting up equations (8) (of figure 1) and the approximate formula (14') for the dependence of $x(z)$, we obtain finally:

$$\left.\begin{aligned}
dn_{dl} &= 0 \qquad \text{at } 0 < l < l_{max} - z_A \\
dn_{dl} &= F(x_N) \cos (\frac{\pi}{2} \frac{l_{max} - l}{z_A}) \cdot \cos hyp (\frac{\pi}{2} \frac{l_{max} - l}{z_A}) \, dl \\
&\qquad \text{at } l_{max} - z_A < l < l_{max} \\
dn_{dl} &= 0 \qquad \text{at } l > l_{max}
\end{aligned}\right\} 20$$

The final distribution of particles by size after the cessation of crystallization is set forth as analogous formulas:

$$dn_{dl} = 0 \qquad \text{at } 0 \leqslant l \leqslant L - z_A$$

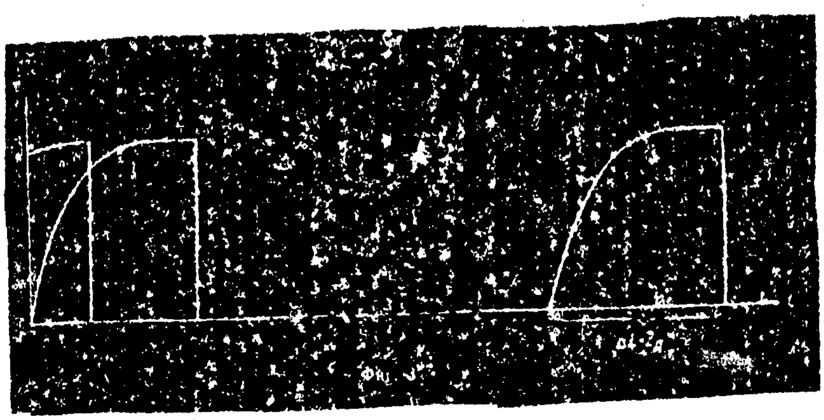
$$dn_{dl} = F(x_N) \cos\left(\frac{\pi}{2}\frac{L-l}{z_A}\right) \cos hyp \left(\frac{\pi}{2}\frac{L-l}{z_A}\right) dl \qquad (21)$$

$$\text{at } L - z_A \leqslant l \leqslant L$$

$$dn_{dl} = 0 \qquad \text{at } l > L$$

The form of the distribution curve $\frac{dn}{dl}$ according to the formulas (20) and (21) is represented for various moments of time in figure 3.

Since according to our assumption $z_A \ll L$, this is represented in figure 3; the sizes of all crystal particles that are close to each other in magnitude also lie in the narrow interval $\Delta l = z_A$, which is much less then the final maximum size of the particles.



B. The total number of particles

The total number of crystal particles forming by a given moment of time is found by the integration of expressions (20) or (21)

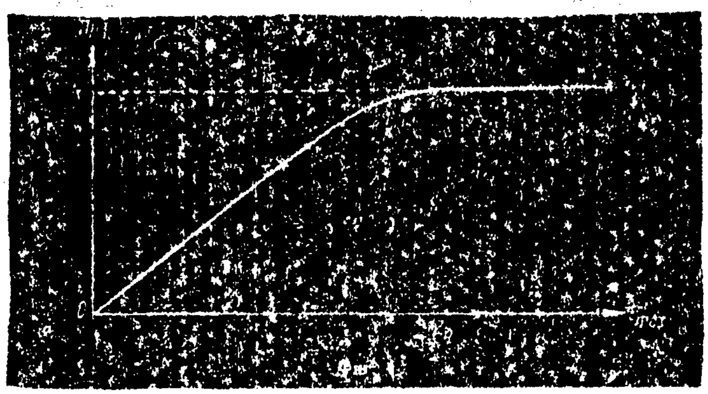
$$n(t) = \int_0^{l_{max}(t)} dn_{dl} \quad . \qquad (22)$$

At $l_{max}(t) = z < z_A$

$$n(l_{max}) = \int_0^{l_{max}} F(x_N)\cos\left(\frac{\pi}{2}\,\frac{l_{max}-l}{z_A}\right)\operatorname{coshyp}\left(\frac{\pi}{2}\,\frac{l_{max}-l}{z_A}\right)dl =$$

$$= F(x_N)\frac{z_A}{\pi}\left\{\cos\left(\frac{\pi}{2}\,\frac{l_{max}}{z_A}\right)\operatorname{sinhyp}\left(\frac{\pi}{2}\,\frac{l_{max}}{z_A}\right) + \right.$$

$$\left. + \sin\left(\frac{\pi}{2}\,\frac{l_{max}}{z_A}\right)\operatorname{coshyp}\left(\frac{\pi}{2}\,\frac{l_{max}}{z_A}\right)\right\} . \qquad (23)$$



At $l_{max} > z_A$ subsequent crystallization practically ceases, and the number of particles remains constant and equal to:

$$N = n(z_A) = \frac{\cos\operatorname{hyp}\frac{\pi}{2}}{\pi}\,F(x_N)z_A \ . \qquad (24)$$

The dependence of n (l_{max}) according to formulas (23) and (24) is represented in figure 4.

C. The time duration of the process

Using the symbols introduced by us the rate of the decrease of concentration in the homogeneous phase is equal to:

$$w = -\frac{dx}{dt} = -\lambda(x)\frac{dx}{dz} \ . \qquad (25)$$

Knowing the dependence of λ on x, and of x on z, it is possible to find the dependence of interest to us, that of w(x) -- the dependence of the rate on the concentration, and by integrating equation (25) the time duration of the process:

$$t = \int_{x}^{x_N} \frac{dx}{\lambda(x)\frac{dx}{dz}} . \tag{26}$$

Under our assumptions the dependence of x on t, exclusive of a small initial interval of time, is expressed with sufficient accuracy by formula (18). Thence:

$$x = x_N \left\{1 - \frac{z^3}{L^3}\right\}; \quad z = L\sqrt[3]{1 - \frac{x}{x_N}};$$

$$\frac{dx}{dz} = -3\frac{x_N}{L^3}z^2 = -3\frac{x_N}{L}\left(1 - \frac{x}{x_N}\right)^{\frac{2}{3}}$$

and

$$w = -\frac{dx}{dt} = 4\frac{x_N^{\frac{1}{3}}}{L}(x_N - x)^{\frac{2}{3}}\lambda(x) . \tag{27}$$

Expression (27) naturally coincides with the dependence investigated in one of our preceding studies, which dependence was developed under the assumption of a total absence of nuclei formation during the time of the entire process of crystallization. If at an initial moment of time one sets, in the solution, n_o as the initial number of crystallization centers with negligibly small dimensions for each, then the rate of decrease of the concentration w will be proportional to the rate of the linear increase of $\lambda(x)$ and to the total surface area of the crystal particles:

$$S(x) = -3\gamma l^2 n_o = 3\gamma \cdot \left(\sqrt[3]{\frac{x_N - x}{n_o}}\right)^2 n_o =$$

$$= \frac{3\gamma^{\frac{1}{3}}}{\rho^{\frac{2}{3}}} n_o^{\frac{1}{3}} (x_N - x)^{\frac{2}{3}} . \tag{28}$$

Inserting (28) in the equation for the rate

$$w = -\frac{dx}{dt} = \rho S(x)\lambda(x)$$

and comparing with (27), we obtain the result that the equivalent initial number of centers n_o will be:

$$n_o = \frac{\cos hyp \frac{\pi}{2}}{2\sqrt[4]{1.5}} \cdot \frac{F^{\frac{3}{2}}(x_N)(x_N - x_A)^{1/4}}{(\gamma\rho)^{1/4}} . \qquad (29)$$

That is, n_o is actually equal to the total number of all crystal particles N forming, in our case, in a very short initial period of time, at a decrease of the supersaturation from x_N to x_A.

4. Discussion of the results obtained

We put together a resume of the quantitative results obtained by us in the preceding paragraphs:

the maximum size of a crystal:

$$L = 0.95\frac{x_N^{\frac{1}{3}}}{(\gamma\rho)^{1/4}(x_N - x_A)^{\frac{1}{12}}} \cdot \sqrt[4]{\frac{\lambda_N}{\alpha_N}} , \qquad (17)$$

the interval of the sizes of crystals:

$$\Delta l = z_A = 1.4\frac{(x_N - x_A)^{1/4}}{(\gamma\rho)^{1/4}} \cdot \sqrt[4]{\frac{\lambda_N}{\alpha_N}} , \qquad (15)$$

and the total number of all crystal particles:

$$N = 1.1\,\frac{(x_N - x_A)^{1/4}}{(\gamma\rho)^{1/4}} \cdot \left(\frac{\alpha_N}{\lambda_N}\right)^{1/4} . \qquad (24^*)$$

The decrease of concentration to the moment of the practical cessation of supersaturation:

$$x_N - x_A = \frac{1}{\varkappa \lg F(x_N)/\alpha x_N} . \qquad (13^*)$$

The maximum rate of decrease of concentration in the homogeneous phase:

$$w_{max} \approx x_N\frac{\lambda_N}{L} \approx (\gamma\rho)^{1/4}(x_N - x_A)^{\frac{1}{12}} x_N^{\frac{2}{3}} \alpha_N^{1/4} \lambda_N^{3/4} \qquad (27^*)$$

(we evaluated the last formula as to order of magnitude from formula (27)). The time to attain the maximum rate

(in order of magnitude):

$$t_{max} \cong \frac{x_N}{w_{max}} = \frac{1}{\lambda_N} \cong \frac{x_N^{\frac{1}{3}}}{(\gamma\rho)^{1/4}(x_N - x_A)^{\frac{1}{12}}\alpha_N^{1/4}\lambda_N^{1/4}} \cdot \frac{1}{} \quad . \quad (26^*)$$

The time for practical cessation of the separating out of crystals:

$$t_A = \frac{z_A}{\lambda_N} = \frac{(x_N - x_A)^{1/4}}{(\gamma\rho)^{1/4}} \cdot \frac{1}{\alpha_N^{1/4}\lambda_N^{1/4}} \quad . \quad (30)$$

From the values determined for α_N, λ_N, and for $(x_N - x_A)$, the probability of nuclei formation α_N depends very sharply on the external parameters (supersaturation, temperature, etc.).

The logarithmic derivative entering into (13) then, in effect, comes down to the logarithmic derivative of α_N

$$x_N - x_A = \frac{1}{d \lg \alpha_N / dx_N} \quad . \quad (13^{**})$$

Employing the formula of Volmer (10), we thereupon obtain

$$x_N - x_A \cong \frac{x_N^3}{20x.^2}, \text{ at low supersaturation}$$

[20x.^{2} may mean 20x$_c$^{2} -- tr] (13***)

$$x_N - x_A \cong \frac{x_N^3 \lg\left(\frac{x_N}{x_o}\right)}{20}, \text{ at high supersaturation}$$

Inasmuch as α_N increases sharply with growth of the initial supersaturation then, as is seen from (17*) and (15*), the quantities L and Δl are also sharply and, approximately, parallel with one another (proportionally to $\alpha_N^{1/4}$) reduced thereby. The total number of particles N, which is proportional to $\alpha_N^{1/4}$, increases sharply with supersaturation. The maximum rate of the process w_{max} increases markedly slowly therein, and the time t_{max} to attain this rate is contracted.

The quantity $x_N - x_A$ varies (increases) significantly slowly with an increase in supersaturation. Thus, our calculation indicates a sharp acceleration of the process and a great increase in dispersion with

increase in supersaturation. The formulas obtained yield not only a qualitative, but also a quantitative picture of this experimentally confirmed phenomenon.

The distribution obtained of particles according to size at the very beginning of the process is almost uniform. Subsequently, however (cf figure 3), it acquires a form little different from the Gaussian error distribution curve.

5. Conclusion

In the development of our preceding studies there was studied in detail the case where the rate of nuclei formation sharply decreases with decrease in supersaturation. A similar dependence arises, for instance, from Volmer's formula (10). Under the assumption advanced all the fundamental characteristics of the process and the form of the distribution curve can be very easily developed.

The curve has a peaked nature and is similar in form to the Gaussian error distribution curve. Computations executed by L. N. Sosnovkin, undergraduate of the Leningrad State University, by means of numerical integration for a particular case of the dependence (10) and for the linear dependence of λ upon x, yielded results practically coinciding with those developed in the present paper.

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